

## PROGRESS ON THE DEVELOPMENT OF A TECHNOLOGY FOR SILICON PURIFICATION

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**ABSTRACT:** The polysilicon market is experiencing tremendous changes due to the strong demand from Photovoltaics (PV), which has by far surpassed the demand from Microelectronics. The need of solar silicon has induced a large increase in capacity, which has now given a scenario of oversupply, reducing the polysilicon price to levels that put a strong pressure on the cost structure of the producers. The paper reports on the R&D efforts carried out in the field of solar silicon purification via the chlorosilane route by a private-public consortium that is building a pilot plant of 50-100 tonnes/year, that will synthesize trichlorosilane, purify it and deposit ultrapure silicon in an industrial-size Siemens type reactor. It has also capabilities for ingot growth and material characterization. A couple of examples of the progress so far are given, the first one related to the recycling scheme of chlorinated compounds, and the second to the minimization of radiation losses in the CVD deposition process, which account for a relevant part of the total energy consumption. In summary, the paper gives details on the technology being developed in our pilot plant, which offers a unique platform for field-testing of innovative approaches that can lead to a cost reduction of solar silicon produced via the chlorosilane route.

**Keywords:** Polysilicon, Solar Silicon, Chlorosilane Route.

### 1 INTRODUCTION

The cost of crystalline silicon PV has experienced a sharp decrease in the last two years, driven by economies of scale and technological improvements in the whole value chain. Improvements such as the increase in ingot size, the use of thinner wafers and the introduction of higher efficiency cell architectures have contributed to reach the \$1/Wp goal and even lower values, which seemed so challenging not so long ago [1]. Polysilicon still accounts for a significant share of the total module cost (15-20% aprox.), even though the silicon utilization has been reduced to around 5-6 g/Wp and the prices have shrunk to \$20-\$30/kg [2].

Until the mid of the last decade, the polysilicon market was a highly concentrated one, with around ten producers worldwide attending the demand from Microelectronics. The fast growth of Photovoltaics increased the demand so strongly (in 5 years the share of polysilicon for solar went from 30% to 85%) that traditional producers were not able to satisfy it, and tens of new producers entered the market promoting different technological approaches, in what seemed a drastic change in the structure of the market. The addition of new capacity (production increased from 30.000 tonnes in 2005 to 200.000 in 2010) and the situation of the PV market have led to an scenario of oversupply, expelling a large number of companies with a non-competitive cost structure and concentrating again the market in a small number of companies (in 2010, five companies accounted for around 70% of the production). Nevertheless, it seems this is a temporary situation, and a new “wave” of solid growth will soon come, which will give opportunities to position in the market to those who manage to be technological prepared to offer high quality polysilicon at a low cost.

The debate on what is the best technological option to produce polysilicon for solar is still open, and several alternatives are being explored, which are typically classified as following the “metallurgical route” or the “chlorosilane route” [3]. What is true is that polysilicon for solar has different constrains in terms of quality and cost as compared to polysilicon for microelectronics, so it makes sense to push R&D&i in this field as there is large room for improvement of current technology. But the big

size of the industrial facilities and the large investments associated with them makes it challenging to validate the promising ideas, making the decisions to scale them up difficult.

### 2 CHLOROSILANE ROUTE FOR SILICON PURIFICATION

The chlorosilane route purifies metallurgical silicon by synthesising a volatile compound that can be further distilled, and then reduce it to solid silicon through a Chemical Vapor Deposition (CVD) process. The traditional process performs the synthesis with HCl in a fluidized bed reactor, and then separates and purifies trichlorosilane, which is then introduced into the so-called Siemens reactor, reacting at high temperature with hydrogen to give the pure polysilicon.

Adaptations of the process to photovoltaic requirements have led to technology costs in the 20-30 €/kg range, and although it is not easy to find contrasted information on the cost structure, the following breakdown can be taken as a reference [4].

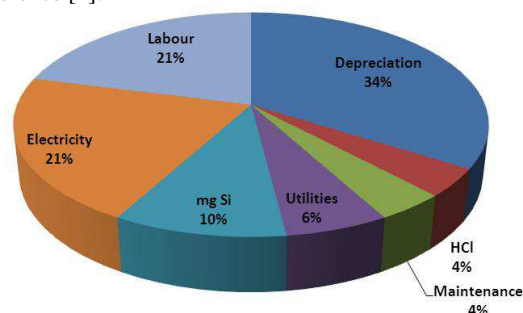


Figure 1. Estimated cost structure for a polysilicon plant, for a total operation cost of around 30 €/kg.

The potential of the technology for cost reduction is by no means exhausted, and proof of that is the long list of aspects being tackled by many research players:

- integrated closed-loop production to recycle by-products and reduce residues;
- increase of productivity, for example by scaling up fluidized bed reactors and other pieces of equipment, or by designing catalysts to soften trichlorosilane synthesis reactions conditions;

- reduction of energy consumption, with special emphasis in the deposition step and in a cost effective heat integration;
- automation of post-processing, and link to crystal growth;
- ...

To address some of these topics, an initiative was launched in 2006 to build a pilot plant, with a size small enough to carry out this complex research, on the one hand, and large enough to ease the transfer to industrial processing, on the other. It is presented in the next section.

### 3 CENTESIL: AND R&D CENTRE ON SILICON PURIFICATION

The Centro de Tecnología del Silicio Solar, CENTESIL, is a private-public partnership venture owned by Universidad Politécnica de Madrid (29.5% of the shares), Universidad Complutense de Madrid (19.5%), and three companies (Isofotón, DCWafers and Técnicas Reunidas, each with 17%).

CENTESIL is currently building a 50-100 t/a pilot plant for silicon purification following the chlorosilane route (see Figure 2). The development contains four areas of activity: (1) synthesis of chlorosilanes, with the silicon tetrachloride, a process by-product, as the main source of chlorine; (2) chlorosilane purification based on fractional distillation; (3) chemical vapor deposition in a Siemens-type reactor implementing strategies to reduce energy consumption and (4) recycling of the by-products for optimal use and sustainability.



Figure 2. Some views of Centesil facilities.

To benefit from an integrated approach, the project includes facilities for ingot growth and wafering, and also the solar cell processing line of the Instituto de Energía Solar.

Although a classical modernized technological path has been selected as first choice, the purpose is to be able

to undertake developments in any topic that has the potential to reduce the cost effectively.

Centesil pilot plant has been already designed, equipment has been constructed or acquired, and is now in the middle of the installation stage, with an additional six months period estimated to be up and running.

In parallel to the installation works, research on some of the key aspects of a polysilicon plant has been tackled. A couple of examples are given in the next section.

### 4 RESEARCH PERFORMED AT CENTESIL: SOME EXAMPLES

#### 4.1. Recycling of light and heavy chlorinated compounds and hydrogen

A thorough study of this point has been conducted since the beginning of the project in order to achieve the maximum atomic efficiency in terms of the ratio of atomic silicon fed to the process to atomic silicon obtained as high quality polysilicon.

Silicon, chlorine and hydrogen losses are related to the amount and type of impurities that are included in the composition of metallurgical grade silicon, used as starting material for polysilicon production. Moreover, these impurities are combined with hydrogen and chlorine in the reactive steps of the process, yielding mixtures of hydrides or chlorides of the impurity elements together with valuable chlorosilanes: trichlorosilane, silicon tetrachloride and dichlorosilane, hydrogen and hydrogen chloride.

To achieve the maximum recovery of pure trichlorosilane, to be used for silicon deposition, a triple synthesis unit, combining traditional trichlorosilane synthesis from silicon metal and HCl, silicon tetrachloride hydrogenation in the presence of silicon metal and dichlorosilane redistribution to trichlorosilane has been considered. A block diagram of the pilot plant is presented in Figure 3.

In this configuration hydrogen chloride and dichlorosilane generated by side reactions in the CVD reactor are recycled to two different synthesis reactors, while the main byproduct, silicon tetrachloride, serves as main source of silicon for trichlorosilane production.

High molecular weight Si-Cl-H compounds, generated during deposition and silicon reaction with HCl, are reactive at high temperatures in the conditions used in hydrogenation reactors. On the other hand, low molecular weight compounds, mainly dichlorosilane, are recycled to a redistribution reactor, in which this compound reacts with recycled silicon tetrachloride, yielding trichlorosilane.

An important starting material in polysilicon production is high purity hydrogen, which is used in big amounts for silicon deposition and also for silicon tetrachloride hydrogenation. Two independent loops for hydrogen recirculation have been proposed and installed in the pilot plant, allowing low consumption of this material.

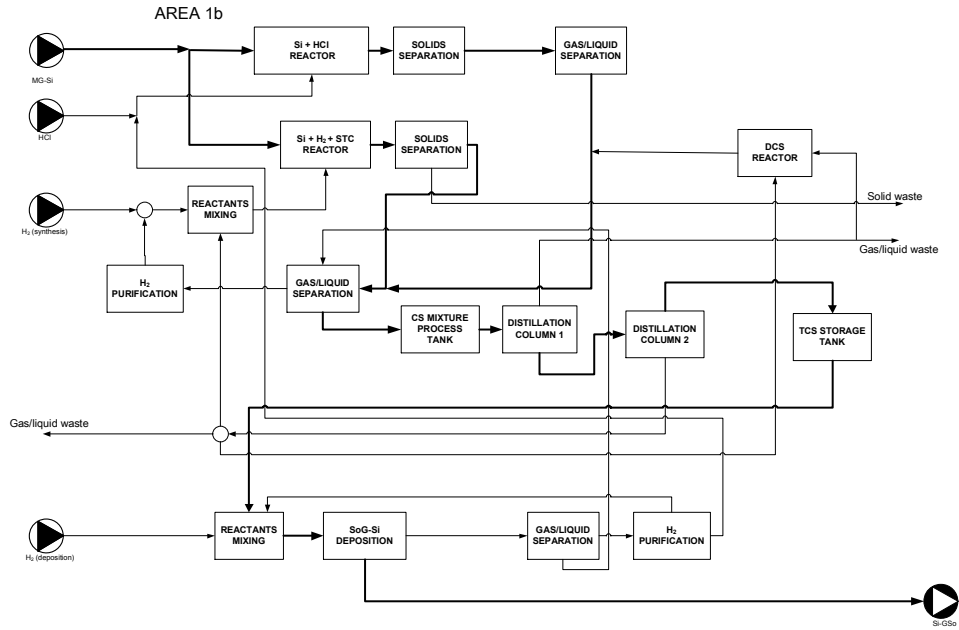


Figure 3. Block diagram of the process installed at Centesil facility.

#### 4.2. Reduction of power losses in CVD deposition

The CVD process is the largest contributor to the energy consumption in the polysilicon production process [5]. Energy losses during the deposition step are due to radiation, convection and chemical reaction. For industrial scale Siemens-type reactors, radiation heat loss is the major responsible for low energetic efficiency of the whole deposition process, and accounts for 65-75% of the total power consumption. Convection losses decrease with the increase of the pressure, and they sum up to 23-33% of the total heat losses. The heat consumed due to the chemical reaction is typically neglected, as it corresponds to less than 1.5% of the total power required [6]. Therefore, in order to reduce the energy consumption of the whole process, the greater energy savings would be achieved diminishing the power loss through radiation.

In our work, a model of radiation heat loss has been developed. The theoretical calculations have been confirmed experimentally using a laboratory prototype CVD reactor at our disposal. All working conditions of the industrial process except the pressure inside the reactor chamber can be reproduced with the prototype, but to extrapolate prototype results to industrial working pressure is straightforward. For the validation of the theoretical model on the basis of empirical experience different scenarios have been, first calculated theoretically, and then reproduced experimentally. The amount of radiated heat loss empirically obtained is very close to the theoretical values, with differences under 8% [6].

Once the model is validated at this prototype scale, it has been applied to the industrial scale. Calculations of the average power emitted per rod and absorbed by the reactor wall for different industrial scale reactor configurations have been already published [7]. Some modeling results are presented in Figure 4, whose analysis indicates that an appropriate thermal shield can save around 20 kWh/kg, while a 60-rod CVD reactor reduces radiation losses 20% as compared to a 36-rod one, which means around 11 kWh/kg energy savings.

Future research work includes the experimental application of all the improvements made in terms of saving power losses through radiation to industrial scale in CENTESIL facilities.

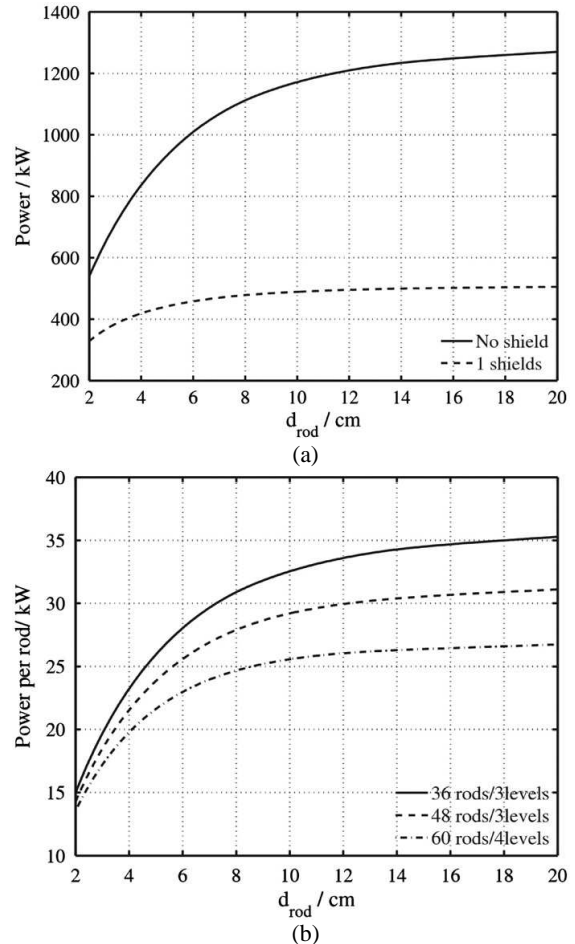


Figure 4. (a) Power radiated by the silicon rods and absorbed by the wall without thermal shields and with one thermal shield in a 36-rod reactor. (b) Average power emitted per rod and absorbed by the reactor wall for different reactor sizes.

## 5 CONCLUSIONS

The chlorosilane route has potential to further reduce the

cost of solar silicon. Centesil is constructing a pilot plant as an R&D platform capable of addressing some of the lines of research and validating them experimentally. In particular, the recycling of chlorinated compounds, and the reduction of radiation losses in the deposition process.

## 6 ACKNOWLEDGMENTS

The Spanish Ministerio de Ciencia e Innovación and the Fondo Europeo de Desarrollo Regional are greatly acknowledged for their support through projects PSE-120000-2007-3, PEN-120000-2009-35 and PCT-420000-2009-17.

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